

## Assessment of sediment contamination at Great Lakes Areas of Concern: the ARCS Program Toxicity-Chemistry Work Group strategy

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**Abstract.** In response to a mandate in Section 118(c)(3) of the Water Quality Act of 1987, a program called Assessment and Remediation of Contaminated Sediments (ARCS) was established. Four technical work groups were formed. This paper details the research strategy of the Toxicity-Chemistry Work Group.

The Work Group's general objectives are to develop survey methods and to map the degree of contamination and toxicity in bottom sediments at three study areas, which will serve as guidance for future surveys at other locations. A related objective is to use the data base that will be generated to calculate sediment quality concentrations by several methods. The information needed to achieve these goals will be collected in a series of field surveys at three areas: Saginaw Bay (MI), Grand Calumet River (IN), and Buffalo River (NY). Assessments of the extent of contamination and potential adverse effects of contaminants in sediment at each of these locations will be conducted by collecting samples for physical characterization, toxicity testing, mutagenicity testing, chemical analyses, and fish bioaccumulation assays. Fish populations will be assessed for tumors and external abnormalities, and benthic community structure will be analyzed. A mapping approach will use low-cost indicator parameters at a large number of stations, and will extrapolate by correlation from traditional chemical and biological studies at a smaller number of locations. Sediment toxicity testing includes elutriate, pore water and whole sediment bioassays in a three-tiered framework. In addition to the regular series of toxicity tests at primary water stations, some stations are selected for a more extensive suite of tests.

### 1. Introduction

#### 1.1. Background

Contamination of sediments in the Great Lakes is a focus of increasing concern. Since 1973 the Great Lakes Water Quality Board (GLWQB) of the International Joint Commission (IJC) has identified 42 sites in the basin as Areas of Concern (AOCs), formerly called 'problem areas'. AOCs are defined as places where beneficial uses of

water resources such as drinking, swimming, fishing, and navigation are impaired (GLWQB, 1989) by anthropogenic pollution or perturbation. In 41 of the 42 AOCs, the IJC has determined that contamination of bottom sediments is a major cause of impairment (GLWQB, 1989). The Great Lakes Water Quality Agreement calls for the establishment of Remedial Action Plans (RAPs) for the restoration of beneficial uses at AOCs. The most recent revision of the Agreement (IJC, 1987) contains a new section, Annex 14, which stipulates

that the U.S. and Canada '... shall, in co-operation with State and Provincial Governments, identify the nature and extent of sediment pollution of the Great Lakes System.' Annex 14 goes on to mandate the development of methods to evaluate both the ecosystem impacts of pollution and the technological capabilities for their remediation. In support of the U.S. commitment to the Great Lakes Water Quality Agreement, Section 118(c)(3) of the Water Quality Act of 1987 calls for the United States Environmental Protection Agency (USEPA), through its Great Lakes National Program Office (GLNPO), to carry out a five-year study and demonstration program for the control and removal of toxic pollutants from the Great Lakes, with emphasis on contaminated bottom sediments. In response to this mandate, GLNPO has established a program called Assessment and Remediation of Contaminated Sediments (ARCS).

Annex 14 and Section 118(c)(3) represent a departure from traditional sediment assessment activities in the Great Lakes Basin. Both documents directly address the problem of contaminated sediments, also known as 'in-place pollutants', outside the traditional context of navigational dredging and dredged material disposal. Concern is now focused on situations where sediments do not necessarily have to be removed to maintain navigational channels, but where sediment contamination, if left in place, presents risks due either to overt toxicity to benthic organisms or to mobility and bioaccumulation in the ecosystem.

### 1.2. *The ARCS Program*

The primary focus of ARCS will be on AOCs. Section 118(c)(3) of the Water Quality Act of 1987 specifically designates five AOCs for priority consideration in choosing sites for sampling and demonstrations: Saginaw Bay (MI), Sheboygan Harbor (WI), Grand Calumet River (IN), Ashtabula River (OH), and Buffalo River (NY). The overall objectives of ARCS are to:

- (1) assess the nature and extent of bottom sediment contamination at priority AOC's;
- (2) evaluate and demonstrate remedial options, including removal, immobilization, and ad-

vanced treatment technologies, as well as the 'no-action' alternative; and,

- (3) provide guidance to various government agencies in the U.S. and Canada on the implementation of RAPs for the AOCs, as well as direction for future evaluations in other areas, on how to assess the need for action and the options available, and how to select appropriate remedial measures.

To address these objectives, GLNPO has established an administrative structure consisting of a Management Advisory Committee (chaired by the GLNPO Director), an Activity Integration Committee (chaired by the ARCS Program Manager), and four technical work groups composed of experts from states, universities, federal agencies, and not-for-profit interest groups. All work group chairs sit on the Activity Integration Committee. The work groups and their mandates are as follows:

- Communications-Liaison Work Group (CLWG) — Facilitate information flow between work groups; promote public participation in the ARCS process. Chair: Glenda Daniel, Lake Michigan Federation, Chicago, IL.
- Toxicity-Chemistry Work Group (TCWG) — Plan and oversee assessments of contamination at priority AOCs; provide guidance for future contamination assessments. Chair: Philippe Ross, Center for Aquatic Ecology, Illinois Natural History Survey, Champaign, IL.
- Risk Assessment-Modeling Work Group (RAMWG) — Assess hazards presented to aquatic and terrestrial biota and human populations under the no-action alternative and also under various remedial option scenarios; from information on the nature and extent of contamination at priority AOCs provide guidance for future hazard assessments. Chair: Marc Tuchman, Region V, U.S. Environmental Protection Agency, Chicago, IL.
- Engineering-Technology Work Group (ETWG) — Evaluate cost and effectiveness of remedial technologies; plan and oversee demonstration projects at priority AOCs; provide guidance for RAP development in future projects. Chair: Steven Yaksich, Buffalo District, U.S. Army Corps of Engineers, Buffalo, NY.

This paper addresses the development of the sediment contamination assessment strategy formulated by the TCWG. It will then introduce the six principal tasks in the strategy. The main body of the paper is devoted to detailed explanations of the major phases of each work unit. The work then concludes with a discussion of some other potential uses of the data base that will be generated. Authorship consists of the original members of the Work Group, as well as other major contributors to the project plan.

## 2. Assessment strategy

### 2.1. Development

Techniques for the assessment of contaminated sediments are still very much in the developmental stage. With the appearance of each new manual or methods document, the state of the art continues to advance. As a starting point the ARCS — TCWG assessment strategy used a manual from the IJC Sediment Subcommittee (IJC, 1988). Stemming from the expertise of the various TCWG members and from recent research developments (Burton *et al.*, 1989; Giesy & Hoke, 1989; Ross & Henebry, 1989), modifications to the IJC approach were proposed and debated. The final strategy represents a consensus of the group and also reflects external constraints due to limitations of time and financial resources. Periodically during the course of the ARCS program, and once again at its termination, the strategy will be re-examined and modified if necessary. At the end of the five-year period, a final guidance document will be published.

### 2.2. Tasks

The TCWG devised an assessment strategy that is similar to the GLWQB (1989) recommendations in that it is based on the integration of physical, chemical, and biological information. To accomplish their assessment objectives, the work group has identified six major tasks:

(1) physical characterization, sampling, and mapping of sediment deposits;

- (2) toxicity testing, mutagenicity testing, and bioaccumulation testing of sediment samples;
- (3) chemical analysis of water, sediment, and fish tissue samples;
- (4) broader-spectrum toxicity testing on a subset of sediment samples;
- (5) fish tumor and external abnormality surveys; and,
- (6) benthic community structure analysis.

Complete performance of all six tasks is possible only at a limited number of stations, due to limitations of time, space, and funding. The TCWG strategy is a compromise entailing a hierarchical array of stations, with a relatively small number of parameters that are measured at all stations. For more detailed study, a smaller number of representative stations is chosen. A nested design results in four levels of analysis for samples at the various stations. These levels are: reconnaissance stations (100 to 200 per AOC), primary master stations (15 to 20 per AOC), priority master stations (8 to 10 per AOC), and extended priority master stations (3 to 5 per AOC) (Fig. 1). The tasks are described in more detail below.

#### 2.2.1. Physical characterization, sampling, and mapping of sediment deposits

The completion of this task requires feedback at several stages, so each survey at a given AOC is broken into five phases: a pre-survey phase; a reconnaissance survey; an inter-survey phase; a supplemental survey; and, a post-survey phase.

*Pre-survey phase:* In the pre-survey phase, existing information on sediment contamination at each AOC to be inventoried will be obtained, reviewed, and transcribed to a map of the site. Based on this, combined with on-site consultations with local experts, a transect — station grid will be prepared to guide sampling and profiling of sediments. Reference points will be located for deploying satellite receivers in a position-finding system for maximum mapping accuracy.

*Reconnaissance survey:* The reconnaissance survey will begin with acoustical profiling along a series of transects that both bisect and follow the river channel. The location of sampling stations (100 to

## TOXICITY/CHEMISTRY ANALYSIS MATRIX

	RECONN- AISSANCE STATIONS	PRIMARY MASTER STATIONS	PRIORITY MASTER STATIONS	EXTENDED PRIORITY MASTER STATIONS
INDICATOR PARAMETERS				
BENTHIC COMMUNITY				
DETAILED CHEMISTRY				
TIERED TOXICITY TESTS				
- <i>Photobacterium phosphoreum</i> - <i>Selenastrum capricornutum</i> - <i>Daphnia magna</i> - <i>Chironomus tentans</i> - <i>Chironomus riparius</i> - <i>Hyalella azteca</i>				
MUTAGENICITY TESTING				
COMPARATIVE TOXICITY TESTS				
- <i>Photobacterium phosphoreum</i> - <i>Selenastrum capricornutum</i> - <i>Daphnia magna</i> - <i>Hyalella azteca</i> - <i>Ceriodaphnia dubia</i> - <i>Lemna minor</i> - <i>Pimephales promelas</i> - <i>Hydrilla verticillata</i> - <i>Diporeia</i> sp. - <i>Hexagenia limbata</i> - <i>Panagrellus redivivus</i> -Bacterial enzymes -Substrate colonization				
BIOACCUMULATION				
- <i>Pimephales promelas</i>				

Fig. 1. Matrix of analyses to be performed (shaded areas) on sediment samples from stations at Great Lakes AOCs under the ARCS program. Four levels of stations are listed, corresponding to the level of effort at each.

200) will be based on the presence of sediment deposits, upon which a sampling grid is imposed. Vertical cores of sediment will be collected from these stations with a Vibra-corer, and the core horizons are visually characterized and photographed. Each 60 cm section of a core will be homogenized and subsampled for analysis of indicator parameters (Table 1; Fig. 2). Vertical characterization will thus proceed in 60 cm intervals.

At each AOC studied, an initial set of surficial sediment samples from primary master stations (8 to 10 locations, about half the eventual total) will be collected before or during the reconnaissance survey, using a Ponar<sup>TM</sup> grab, which samples the surface sediment to a depth of approximately 20 cm. Some of these primary master stations will be designated, on a percentage basis, as priority master stations, and some of those will in turn be chosen, again on a percentage basis, as extended

Table 1. Indicator parameters to be analyzed at all ARCS stations

- Sediment grain size distribution
- Wet weight
- Dry weight
- Ash weight
- Organic carbon
- Solvent extractable residues
- Organically bound chlorine, bromine and iodine
- Inductively coupled plasma (ICP) analysis of selected metals
- Microtox<sup>TM</sup> bacterial luminescence assay response

priority master stations. These station-level designations must be made before sampling, because of the different volumes of sample required for the different levels of effort. Sediment samples will be homogenized, split, and transported to participating laboratories for physical, chemical, and biological testing (Fig. 1).

*Inter-survey phase:* Indicator parameter data from reconnaissance station samples will serve two purposes. First, these data will help to identify areas where additional primary master stations should be located. Second, the indicator parameter data will expand the resolution of sediment mapping. The indicator parameters will be strongly correlated with other, more sophisticated measurements of contamination and toxicity. Use of indicator parameters (Table 1) will thus allow the detailed analyses from the relatively small number of primary master stations to be extrapolated over a larger area, based on correlations between reconnaissance and primary master station data. Information from this analysis and from acoustical profiling data obtained during the reconnaissance survey will be used to prepare preliminary three-dimensional maps of contaminants and effects (Fig. 3). Maps of bottom topography and sediment layer thickness will also be prepared. Based on this information the remaining master stations will be identified for sampling during the supplemental survey.

*Supplemental survey:* Sediments from the remaining primary master stations are collected, homogenized, and shipped to laboratories for chemical and biological characterization. Additional Vibra-

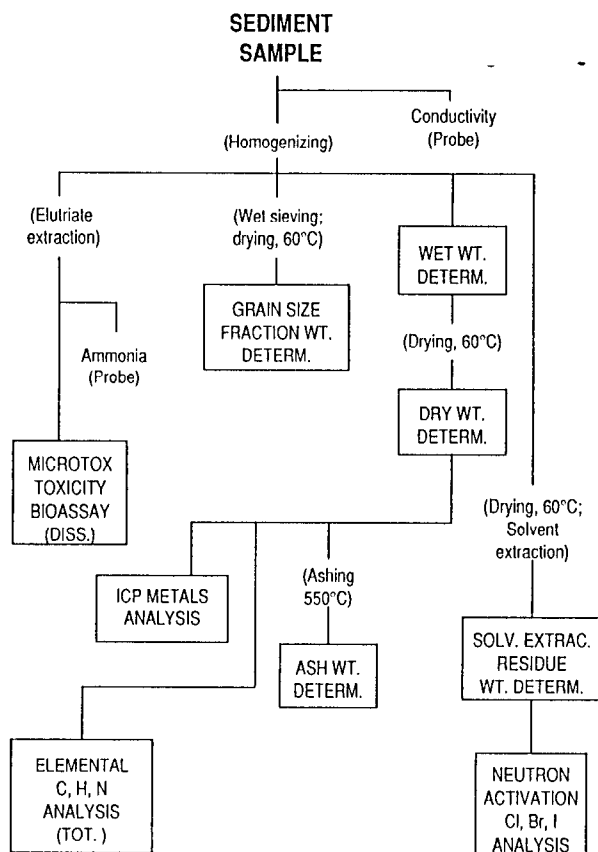


Fig. 2. Schematic procedure for indicator analysis of sediment samples at reconnaissance stations.

cores, if required for clarification of ambiguities found in previous surveys, are also collected at this stage.

**Post-survey phase:** The three-dimensional sediment, toxicity, and contaminant distribution maps will be refined and completed, using toxicity test data from master stations as base points and extrapolating to secondary map points with correlated data from reconnaissance stations.

#### 2.2.2. Toxicity testing and mutagenicity testing of sediment samples

Laboratory testing of sediment samples from primary master station will follow a tiered approach. Tier I testing will focus on acute toxicity and mutagenicity assays. Tier II employs partial life-cycle testing, while Tier III will emphasize full

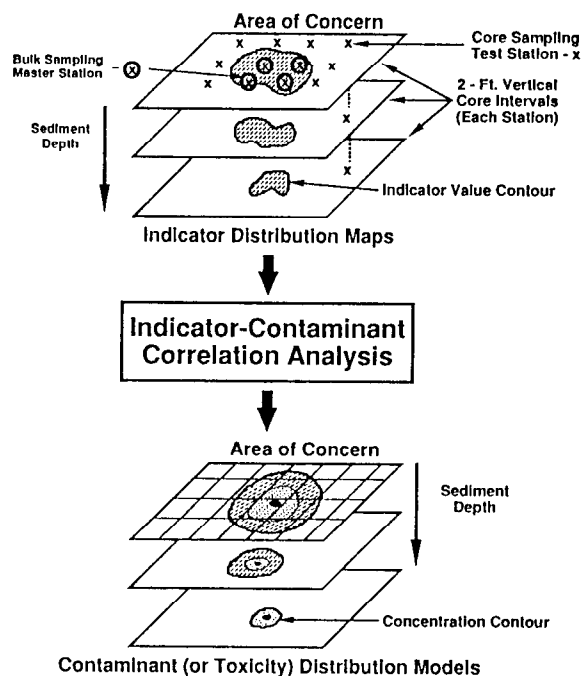


Fig. 3. Process of mapping sediment contamination and toxicity, using a relatively large number of reconnaissance stations, where indicator parameters are measured, and a much smaller number of master stations.

life-cycle toxicity. All primary master station samples will undergo Tier I testing, using the following biological tests:

- *Daphnia magna*, — 48 h mortality test — elutriate phase.
- Microtox™ (*Photobacterium phosphoreum*) — luminescence test — elutriate phase.
- *Selenastrum capricornutum* — 24 h carbon-14 uptake test — elutriate phase.
- Ames mutagenicity test — organic extract.
- Mutatox test — organic extract.

In all tests, reference experiments will be performed with whole-sediment exposures or elutriate tests using a reference material, the Florissant (MO) top-soil deposit (Ingersoll & Nelson, 1990). Approximately 50 percent of the samples undergoing Tier I testing will be selected for Tier II testing, which consists of the *Hyaella azteca*, *Chironomus tentans*, and *Chironomus riparius* 7- to 14-day, whole sediment survival and growth

tests. Up to 25 percent of the primary master station samples will go on to Tier III testing. Tier III consists of the *H. azteca* 28-day (whole sediment) survival, growth, and reproduction test. Selection of samples for Tiers II and III will be made with two considerations. First, samples with low acute toxicity will form the majority of the selections, as the purpose of tiered testing is to look for more subtle effects than can be shown in the first tier. Second, some samples with moderately acute toxicity and some with highly acute toxicity will be included, to provide an appropriate range over which to evaluate the tiered testing system. Since some of each sediment sample must be held before selection for Tiers II and III, the Microtox™ bacterial test will be used to monitor for changes in toxicity during holding.

At extended priority master stations, a 10-day fathead minnow (*Pimephales promelas*) bioaccumulation assay will be conducted using bulk sediment samples. Chemical analysis of the fish tissue is conducted as described below.

#### 2.2.3. Chemical analysis of sediment and fish samples

The approach for chemical analyses of sediment and fish tissue samples is intended to permit flexibility in the analytical process. Rather than intentionally searching for an initial list of specifically named individual chemicals in each sample, extraction and analysis procedures for groups of chemicals and detection limits for chemicals in each type of extract will be specified. The desired precision will thus be obtained for all individual chemicals present in detectable amounts, but without needless searches for contaminants that may not exist in a given sample. The chemical laboratory must experiment and make adjustments in the course of the study. Chemical parameters and groups to be studied are listed in Table 2.

#### 2.2.4. Broader-spectrum toxicity testing on a subset of sediment samples

One of the TCWG objectives is to provide guidance for future contamination surveys. It is necessary to compare the performance of as many biological tests as possible. It is not feasible to perform all available tests on all primary master station samples, due to constraints of cost, space,

Table 2. Chemical parameters and compound groups to be studied in primary master station samples and fish tissues from bioaccumulation tests

- 
- Sediment Organic Carbon
  - Free and Acid Volatile Sulfides
  - Extractable metals
  - Heavy Metals — Ag, As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Se and Zn in pore water, elutriates and whole sediment samples
  - Organo-metals — methyl mercury and butyl tin
  - Polynuclear Aromatic Hydrocarbons — about 16 compounds
  - Polychlorinated Biphenyls — about 20 congeners
  - Chlorinated Pesticides
  - Chlorinated Benzenes
  - Chlorinated Naphthalenes
  - Chlorinated Dioxin and Furan congeners
  - Volatile Chlorinated Compounds
- 

and personnel. A strategy for making such comparisons is to perform additional toxicity tests on samples from a reduced number of stations, designated as priority master stations. To implement this approach, a consortium of laboratories with recognized expertise in numerous other testing methods has been assembled. Sediments from priority master stations will be homogenized and divided for distribution to these investigators for a broader series of tests. The resulting information will be compared to results from the primary master stations. Several of the additional toxicity tests will also yield dose-response information, and some of the tiered-system tests repeated, to provide a Quality Assurance comparison. In total, 15 toxicity test systems and 31 individual endpoints (Table 3) will be studied by a consortium of laboratories (Great Lakes Environmental Research Center, Illinois Natural History Survey, Memphis State University, National Fisheries Research Center — Great Lakes, National Fisheries Contaminant Research Center, Wright State University, and the University of Minnesota).

#### 2.2.5. Fish tumor and external abnormality surveys

Existing information on the incidence of external abnormalities and internal tumors in fish at each priority consideration AOC will be researched. In addition, field surveys to determine tumor and abnormality incidence will be conducted. For each

Table 3. Biological tests used in the TCWG study program

Test system	Medium	Endpoint	Duration
<b>A. Toxicity tests</b>			
<i>Photobacterium phosphoreum</i> Harvey	Elutriate	Function	15 min
<i>Selenastrum capricornutum</i> Printz	Elutriate	Function	24 h
	Elutriate	Growth	48 h
<i>Daphnia magna</i> Straus	Elutriate	Mortality	96 h
	Sediment	Mortality	48 h
	Sediment	Reproduction	7 d
<i>Chironomus tentans</i> Fabricius	Sediment	Mortality	10 d
	Sediment	Growth	10 d
<i>Chironomus riparius</i> Meigen	Sediment	Mortality	14 d
	Sediment	Growth	14 d
<i>Hyalella azteca</i> Saussure	Sediment	Mortality	7 d; 14 d; 28 d
	Sediment	Growth	14 d; 28 d
	Sediment	Reproduction	14 d; 28 d
<i>Ceriodaphnia dubia</i> Richard	Elutriate	Mortality	48 h
	Elutriate	Reproduction	7 d
	Sediment	Mortality	48 h
	Sediment	Reproduction	7 d
<i>Lemna minor</i> L.	Sediment	Growth	48 h
	Sediment	Structure	48 h
<i>Pimephales promelas</i> Rafinesque	Sediment	Mortality	7 d
	Sediment	Growth	7 d
	Sediment	Terata	7 d
<i>Hydrilla verticillata</i> Royle	Sediment	Growth	14 d
	Sediment	Function	4 d; 7 d
	Sediment	Structure	4 d
<i>Diporeia</i> sp. Bousfield	Sediment	Mortality	28 d
<i>Hexagenia limbata</i> Serville	Sediment	Growth	28 d
	Sediment	Mortality	28 d
<i>Panagrellus redivivus</i> L.	Elutriate	Growth	4 d
Bacterial enzymes	Sediment	Function	2 h
Artificial Substrates	Sediment	Comm. structure	28 d
<b>B. Other biological tests</b>			
<i>Salmonella typhimurium</i> Castellani Chalmers	Org. extract	Mutation	72 h
<i>Photobacterium phosphoreum</i> Harvey	Org. extract	Mutation	12 h
<i>Pimephales promelas</i> Rafinesque	Sediment	Bioaccumulation	10 d
<i>Ictalurus nebulosus</i> LeSueur	Sample	Tumors	Collection
Benthic community	Sample	Comm. structure	Collection

survey 100 individual fish will be collected and targeted for field necropsy and subsequent histopathological examination. The brown bull-head (*Ictalurus nebulosus*) is the primary study species, with the white sucker (*Catostomus commersoni*) serving as an alternative.

#### 2.2.6. Benthic community structure analysis

At each AOC in the study, a literature search for existing information on the structure of benthic

communities is conducted. A benthic survey is conducted using samples from primary master stations. Analyses include species occurrence, abundance and diversity, as well as multivariate metrics of community structure.

#### 2.3. Additional aspects

In addition to the mapping of contaminant and toxicity distributions, data from the AOC surveys

are used for modeling and risk assessment purposes. When data from all AOCs have been generated, the TCWG will have an integral set of chemistry, toxicity, mutagenicity, and benthic community structure data from about 40 primary master stations. With this data base, several methods for generating Sediment Quality values, such as Equilibrium Partitioning, the Apparent Effects Threshold, Screening Level Concentrations, and the Sediment Quality Triad, will be applied to evaluate the relative performance of these methods in freshwater ecosystems.

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